TiO$_2$ Nanoparticles with Tetra-pad Shape Prepared by an Economical and Safe Route at very Low Temperature

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Abstract

We report an organics free and safe route for the preparation of titanium dioxide (TiO$_2$) nanoparticles having tetrapad shape. The approach is based on a very simple reaction of titanium powder and de-ionized water at very low temperatures of ~140°C without using any organics or surfactants. By the morphological investigations using FESEM and HRTEM, it was observed that the grown products are having tetrapad shape with the diameters in the range of 10-50nm. The EDS and XRD pattern confirmed the composition and crystallinity of the grown nanoparticles and revealed that the grown products are pure TiO$_2$ with the tetragonal anatase phase. Since only water, which is regarded as a benign solvent is used during the preparation of nanoparticles, we believe that the product so produced is biocompatible and bio-safe and can be readily used for food and medicine. Besides other advantages, the present method is economical, fast, low temperature, free of pollution and environmentally benign which will make it suitable for large scale production.

Keywords: De-ionized water, Titanium powder, Bio-safe synthesis, Nanoparticles

1. Introduction

As a promising photocatalyst, titanium dioxide (TiO$_2$) materials are playing a significant role in helping to solve many serious environmental and pollution challenges. TiO$_2$ also bears tremendous hope in helping ease the energy crises through effective utilization of solar energy based on the photovoltaic and water splitting devices (Chen X, Mao, S.S, 2007). It is widely used as photocatalyst due to its relatively cheap cost, non toxicity and high chemical stability. As a photocatalyst, it is used for the decomposition of various organic pollutants. Compared to other semiconducting photocatalysts, TiO$_2$ has been proven to be the most preferable material for photocatalytic processes due to its biological and chemical inertness, high photoreactivity, non toxicity and photostability (Asahi R, Morikawa, T, Ohwaki T, Aoki K, Taga Y, 2001). Due to its wide band gap (3.2 eV for

anatase), TiO_2 can be excited only with UV light (390nm), which accounts for only a small fraction of solar light (3-5%). The photocatalytic performance of TiO_2 particles are highly related with the particle size and shape. The quantum size effect becomes significant in the photocatalysis of TiO_2 particles when the particle size is smaller than 30nm, leading to the widening of the band gap and thus to the enhancement of redox ability of photo generated electron hole pairs (Crap O, Huisman, C.L, Reller A, 2004). New physical and chemical properties emerge when the size of materials becomes smaller and smaller, and down to the nanometer scale. Properties also vary as the shape of the shrinking nanomaterials change (Shah, M.A, Towkeer, A. 2001).

Among the unique properties of nanomaterials, the movement of electron and holes in the semiconductor nanomaterials is primarily governed by the well known quantum confinement and the transport properties related to phonons and photons are largely affected by the size and geometry of materials. The specific surface area and surface to volume ratio increase dramatically as the size of materials decreases. The high surface area brought about by small particle size is beneficial to many TiO_2 based devices as it facilitates reaction /interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface and strongly depends on the surface area of the material. Thus the performance of TiO_2 based devices is largely influenced by the sizes of TiO_2 building units, apparently at the nanometer scale (Zhang J, Xiao X, Nan J, 2010).

TiO_2 have been generated by physical methods, chemical approaches have proved to be more effective and efficient as they provide better control over the size and shape, which is one of the essential requirements for the preparation of nanomaterials. Chemical synthesis of nanomaterials has been reviewed by few authors but innumerable improvements and better methods are being reported continually in the last few years. Cassaignon et al. (Cassagnon S, Koelsch M, Jolivet, J.P, 2007) reported selective synthesis of brookite, anatase and rutile nanoparticles by the thermo-hydrolysis of TiO_4 in concentrated aqueous nitric acid, wherein the selectivity was strongly dependent the medium acidity. Similarly, using aqueous solutions of TiO_4 and acidic additives, Yin et al. (Yin H.B, Wada Y, Kitamura T, Sumida T, Hasegawa Y, Yanagida S, 2002) and Franklyn et al. (Franklyn P.J, Levendis D.C, Demetrius C, Coville N.J, Maaza M, 2007) confirmed the selective formation of nanoparticulate anatase and rutile nanorods. In addition, Jiu et al. (Jiu J.T, Isoda S, Wang F.M, Adachi M, 2006) reported the synthesis of a pure, highly crystalline anatase phase through hydrolyzing titanium isopropoxide rather than a $TiCl_4$ precursor in presence of ethylenediamine basic catalyst and cetyltrimethylammonium bromide (CTAB) surfactant. Li et a. (Li X.L, Peng Q, Yi J.X, Wang X, Li Y.D, 2006) synthesized TiO_2 nanorods by adding $Ti(OBu)_4$ into the mixed solution of linoleic acid, triethylamine and cyclohexane and then sealing the solution for two days. All of the aforementioned investigations have used organics, surfactants and catalysts during synthesis at very high temperatures. The addition of catalysts or templates of the reaction system involves a complicated process and may result in impurity in the products. Moreover, most of the pathways suggested for the synthesis of nanocrystals involve environmentally malignant chemicals which are toxic and not easily degraded in the environment. Organic solvents are practically problematic because many are toxic which makes the nanomaterials useless. Environmental friendly chemical synthesis requires alternative solvents such as ionic liquids, liquid and water. Water is particularly attractive because it is inexpensive, environmentally benign and bestowed with many virtues (B. Verianshyah, T.J. Park, J. S. Lim, Y.W Lee, 2005).

Recently, an interesting and encouraging result obtained by the reaction of nickel metal with water by Shah and Haq (Shah M.A, Ahsanulhaq, Q, 2009) provides motivation to synthesize TiO_2 nanostructures without additives or organics at low temperatures. Interestingly, nanoparticles with altogether tetrapad shape were obtained by a simple reaction of titanium powder and de-ionized water at very low temperature of $140^{\circ}C$. The grown nanoparticles were characterized in detail in terms of their structural properties. The typical diameters of the as-grown nanoparticles are $\sim 30 \pm 20$ nm. To the best of our knowledge, the synthesis of nanoparticles without organics, catalyst and toxic solvents has not been reported so far. The reported method besides being organics free is economical, fast, environmentally benign and free of pollution, which will make it suitable for large scale production.

2. Experimental

2.1 Materials

Titanium powder (titanium powder, Ranbaxy, > 5μm) was used as a source of titanium and was cleaned by ultra-sonication in acetone and water for 20 minutes in each solvent. The de-ionized water used was prepared in the laboratory.

2.2 Syntheses of TiO₂ nanoparticles

A closed cylindrical Teflon lined stainless steel chamber was used. In a typical preparation process, 10 mg of titanium powder was added to 40 ml of distilled water in a glass vial. The reaction mixture was sonicated for

about 25 minutes in a glass veil, transferred into a stainless steel Teflon lined metallic bomb of 100ml capacity and sealed under inert conditions. The closed chamber was then placed inside a preheated box furnace and the mixture was heated slowly (2^oC/min) to 140^oC and maintained at this temperature for 12 hours. The furnace is allowed to cool after the desired time and the resulting suspension was centrifuged to retrieve the product, washed and then finally vacuum dried for few hours.

2.3 Characterization of TiO_2 nanoparticles

The morphology and the size of the products was carried out using high resolution FE-SEM (FEI NOVA NANOSEM-600) coupled with energy dispersive x-ray spectrometer (EDX). The features and shapes of the particles were also imaged by Transmission Electron Microscope (TEM, JEM-2010HR, Jeol Japan) operated at 200kV. The phase composition of the as synthesized samples were identified by X-ray diffraction on a Siemens D 5005 diffractometer using Cu Kα (λ =0.15141 nm) radiation operated at 30kV and 30mA. The crystallite size of particles were also calculated using Scherer equation d = kλ/βcosθ, where k is constant, λ wavelength of X-rays and β is the full width half maximum (FWHM) for (111) reflection.

3. Results and discussion

The general morphologies of the as-grown structures, obtained after the reaction of titanium powder with de-ionized water at 140^oC for 12h, was observed by FESEM and shown in figure 1. By the morphological investigations using FESEM, it was observed that the grown products are nanoparticles with an average diameter of ~25nm. Figure 1 (a,b) and (c,d) show the low and high magnification FESEM images of the nanoparticles and confirms that the nanoparticles are grown in a very high density having shape of tetrapad. The HRTEM confirmed the morphology and size of the particles as shown in figure 2.

To check the composition of the as-grown nanoparticles, EDX analysis was performed. Figure 3 demonstrates the typical EDX analysis of the as-grown TiO_2 nanoparticles. It is confirmed from the EDX analysis that the grown nanoparticles are composed of titanium and oxygen only. The molecular ratio of Ti:O of the grown nanoparticles, calculated from EDX and quantitative analysis data, is close to that of bulk. Except Ti and O, no other peak for any other element has been found in the spectrum which again confirmed that the grown nanoparticles are pure TiO_2.

Structural information of the final product could be given by powder X-ray diffraction (XRD) analysis. In the XRD pattern of sample (figure 4), all the observed peaks can be indexed to a pure tetragonal anatase phase (JCPDS card, 21-1272) with lattice constants a = 3.785 A ° and c = 9.513A°. No peak of other phases was observed, which indicates that the product is pure and well crystallized.

The formation of TiO_2 nanoparticles on titanium foil in the presence of water can be explained by chemical reactions. As initially, titanium does not react with water molecules but at 140°C and under pressure in Teflon-lined stainless chamber, the titania reacted with water and forms a protective titanium hydroxide ($Ti(OH)_2$) layer with dissolved hydroxide ions onto the surfaces of the titanium particles according to the following reaction mechanism:

$$Ti^{2+} + 2OH^- \xrightarrow{\triangle} Ti\,(OH)_2 \qquad (1)$$

Moreover, as the concentration of the Ti^{2+} and OH^- ions exceeds a critical value, the precipitation of TiO_2 nuclei starts. The $Ti(OH)_2$ can be transformed into the TiO_2 crystals via the simple chemical reactions mentioned below:

$$Ti\,(OH)_2 \xrightarrow{\triangle} TiO_2 + H_2O \qquad (2)$$

The precipitates of $Ti(OH)_2$ are more soluble as compared to the TiO_2 precipitates, therefore, the formed $Ti(OH)_2$ precipitates tend to continuously produce Ti^{2+} and OH^- ions which form the TiO_2 nuclei. The formed TiO_2 nuclei are the building blocks for the formation of the final products as shown schematically in figure 5. Moreover, water at elevated temperatures plays an essential role in the precursor material transformation because the vapor pressure is much higher and the state of water at elevated temperatures is different from that at the room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures and high pressure is favorable for crystallizations (Wang W, Gu B.H, Liang L.Y, 2004). There have been reports that excellently discussed the possible mechanism of the anatase and rutile formations (Wang Y.W, Zhang, L.Z, Deng K.J, Chen X. Y, Zou Z.G, 2007)(Chen X.B, Mao, S.S, 2006)(Huang Q, Gao L, 2003).

The basic unit of (TiO62−) octahedral in solution can join together to form oligomers which are the growth units leading to both anatase and rutile phases. The joining of the basic octahedral unit if takes place at the opposite edges will give a growth units for the rutile phase, however, if it takes place at the non-opposite edges will give a growth unit for the anatase phase (and possibly the brookite phase, too). The key to the differences in anatase and rutile formation stems from the structure of two polymorphs. In rutile, two opposite edges of each (TiO62−) octahedral are shared forming a linear chain along the (001) direction. Chains are then linked to each other by sharing corner oxygen atoms. Anatase has no corner sharing, but has four edges shared per octahedron. The anatase structure can be viewed as zigzag chains of octahedral, linked to each other through shared edges. From our experiments and analysis, it suggests that the growing mechanism of TiO_2 nanoparticles may be simple hydrothermal process, but it still have large space to be studied.

4. Conclusions

We report a very versatile, non toxic and bio-safe approach for the synthesis of TiO_2 nanoparticles at 140^oC without using any organics. The proposed single source and catalyst free method is simple, soft, economic and environmentally benign which will make it suitable for various applications. Furthermore, it is well expected that such a technique would be extended to prepare many other important metal oxide nanostructures.

Acknowledgement

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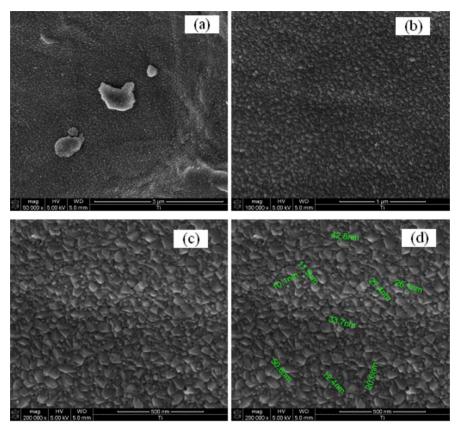

Figure 1. the typical (a and b) low and (c and d) high-resolution FESEM images of TiO$_2$ nanoparticles obtained by the reaction of titanium metal powder with water at 140°C for 12h.
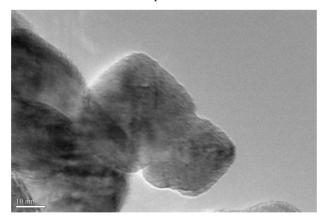

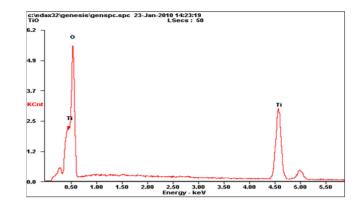Figure 2. The TEM micrograph of TiO$_2$ nanoparticles

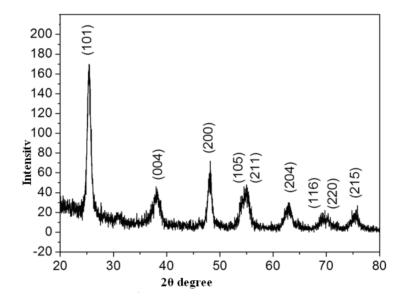Figure 3. The EDX pattern of titanium dioxide nanoparticles

Figure 4. The XRD pattern of TiO_2 nanoparticles

Figure 5. shows a schematic illustration of the growth (a) Ti particles and water vapour co-exists.
(b) Layer of $Ti(OH)_2$ formed on the particle surface and subsequent decomposition to TiO_2.